Asymmetric Diels-Alder Reactions Using Chiral α,β-Unsaturated Sulfoxides as Efficient Dienophiles

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Abstract : This review reports on our recent studies on asymmetric Diels-Alder reactions of chiral α,β-unsaturated sulfoxides. For the preparation of these sulfoxides as Diels-Alder dienophiles, the Andersen method as well as a novel route by diastereoselective oxidation of 2-*exo*-hydroxy-10-bornyl vinyl sulfides with 3-chloroperoxybenzoic acid is presented. The latter methodology has been successfully applied to synthesis of two types of novel sulfoxides bearing labile fuctionality, *i.e.*, α-sulfinylmaleate and α-sulfinylmaleimide derivatives. These sulfinyl dienophiles effect Diels-Alder reactions with a high degree of diastereoselectivity. Especially, the chiral α-sulfinylmaleimides readily react with Diels-Alder dienes of rather low reactivity, to give the corresponding cycloadducts under conventional conditions. Also described are applications of these asymmetric Diels-Alder reactions to natural product synthesis.

Key phrases : chiral α,β-unsaturated sulfoxides; asymmetric Diels-Alder reaction; 2-*exo*-hydroxy-10-bornyl group; chiral auxiliary

Introduction

Chiral α,β-unsaturated sulfoxides have provided useful methods for asymmetric carbon-carbon bond formations.[1] The reason for the use of the sulfinyl functionality as a chiral auxiliary relies on the fact that the differences of steric and electronic effects of the three ligands (usually *p*-tolyl group, oxygen and lone pair electrons) at the sulfur atom may cause the effect of asymmetric induction. The olefin part bonded directly to the chiral sulfoxide function has been shown to be an effective reactive site for an electrophile: some representative examples are illustrated in Scheme 1.

On the other hand the use of the olefinic part in α,β-unsaturated sulfoxides as Diels-Alder dienophiles is also very attractive because the Diels-Alder reaction is the most fascinating strategy for creating up to four chiral centers in one step. Thus, studies on the Diels-Alder cycloadditions using chiral sulfoxides as dienophiles have gained widespread attention during the past decade.[5]

This review will attempt to highlight findings of our recent studies on asymmetric Diels-Alder

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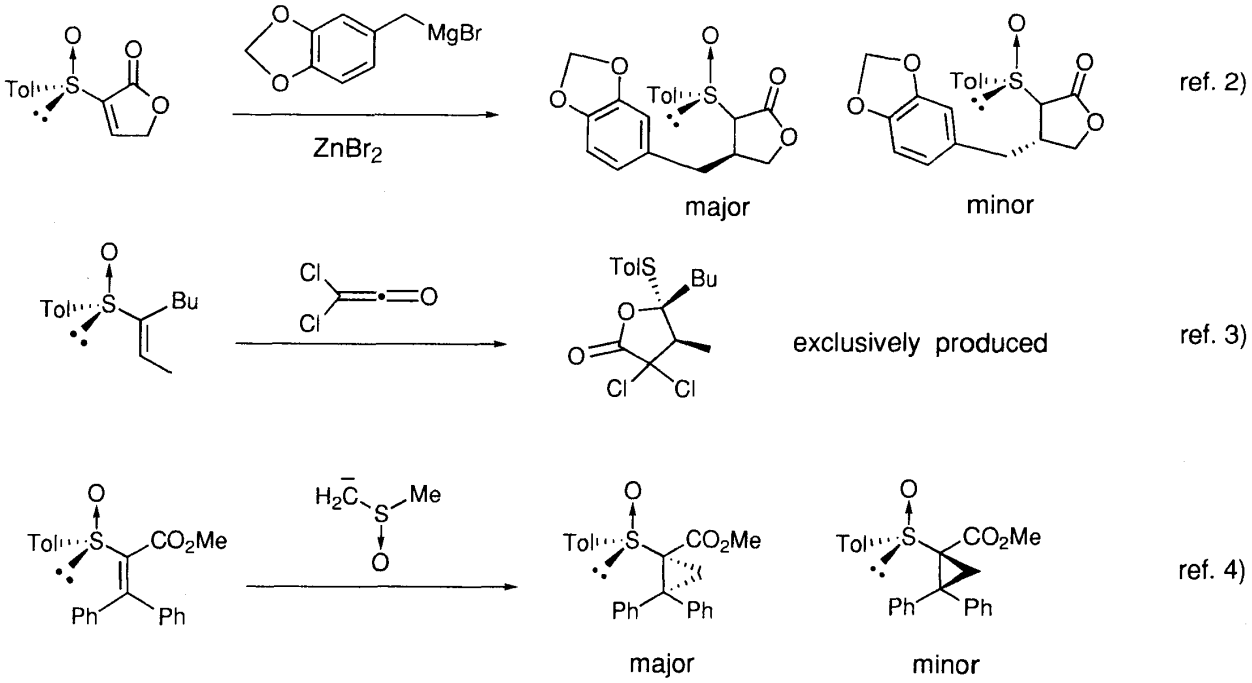
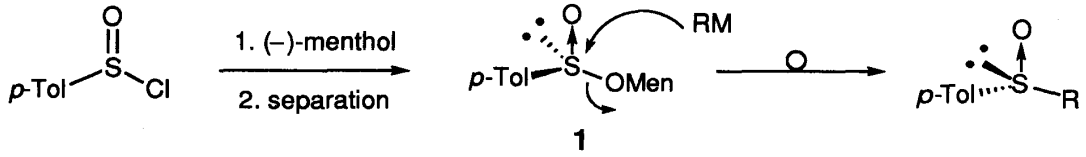
reactions using chiral α, β-unsaturated sulfoxides as efficient dienophiles. The applications to natural product synthesis are also presented.



Scheme 1

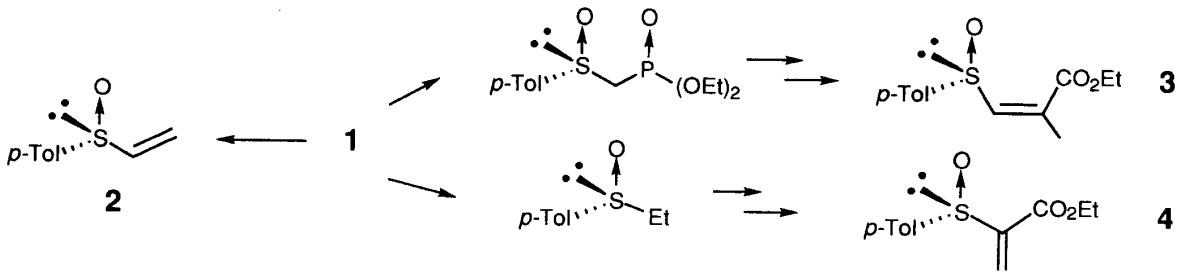
1. Asymmetric Diels-Alder Reactions of *p*-Tolyl α, β-Unsaturated Sulfoxides

As shown in Scheme 1, it is worth noting that a *p*-tolyl group as a ligand of the sulfur center in chiral sulfoxides has been widely employed. It should originate from the fact that the Andersen method is familiar for the preparation of chiral sulfoxides since it has an advantage in that the substitution of (*S*)-menthyl *p*-tolylsulfinate **1**[7] takes place with 100% inversion of configuration (Scheme 2).



Scheme 2

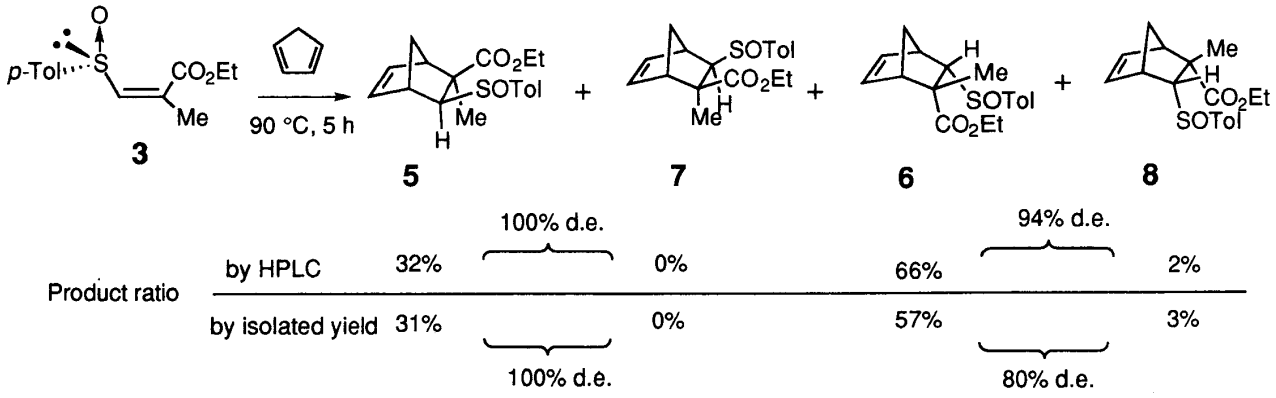
At the outset, we envisaged the Diels-Alder reactions of the *p*-tolyl α, β-unsaturated sulfoxides **2**-**4**, prepared by the Andersen method, with cyclopentadiene (Scheme 3). Especially for sulfoxides **3** and **4**, it was expected that the dienophilicity was enhanced by an additional alkoxycarbonyl group and that the diastereoselectivity was improved by controlling the



Scheme 3

conformational preference due to the dipole-dipole interaction between the sulfinyl and the alkoxycarbonyl group (*vide infra*).

Although the reactivity of the sulfoxide **2**[8] toward cyclopentadiene was poor since the sulfinyl group in **2** may not activate the dienophilicity of the olefinic part, α- and β-alkoxycarbonyl vinyl sulfoxides (**3**[9] and **4**[10]) showed high reactivity (Schemes 4 and 5).



Scheme 4

It can be plausibly explained in terms of steric factors by the mechanism[11] shown in Fig. 1 and Fig. 2. In the case of **3**, the ester would take a predominantly more stable conformer **B** due to the dipole-dipole repulsion. Thus, cyclopentadiene should approach, in exo and endo modes, from the less-hindered lone-pair side to give the two major *exo*-sulfinyl and *endo*-sulfinyl adducts (**5** and **6**). The absolute configuration of **5** was proven by transformation into the known compound. The major *endo*-sulfinyl product **6** is employed in the synthesis of (+)-epi-β-santalene.[9]

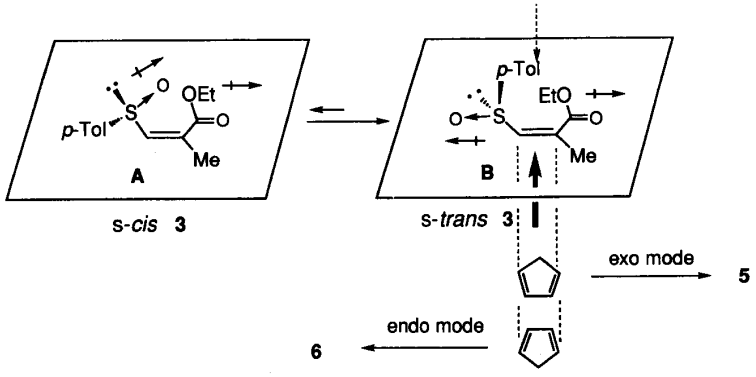
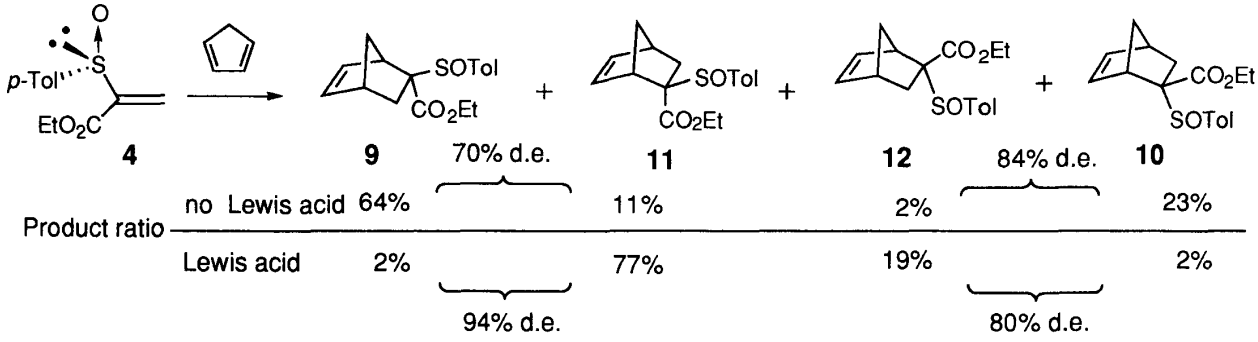


Fig. 1

On the other hand, without a Lewis acid, the reaction of **4** and cyclopentadiene afforded the adducts **9** and **10** as the major *endo*- and *exo*-sulfinyl products (Scheme 5). It can be explained that cyclopentadiene would attack the less-hindered face of more stable conformer **C** in **4**, resulting in the formation of the two major products **9** and **10** (Fig. 2). In turn, in the presence of a Lewis acid ($ZnCl_2$), the two major adducts **11** and **12** were obtained by the reaction. The chelation of S→O with C=O in the dienophile **4** should freeze the rotation around the bond between C=C and S→O, resulting in the favorable conformer **D**. The *endo*- and *exo*-sulfinyl adducts **11** and **12** are thus obtained as the major products.



Scheme 5

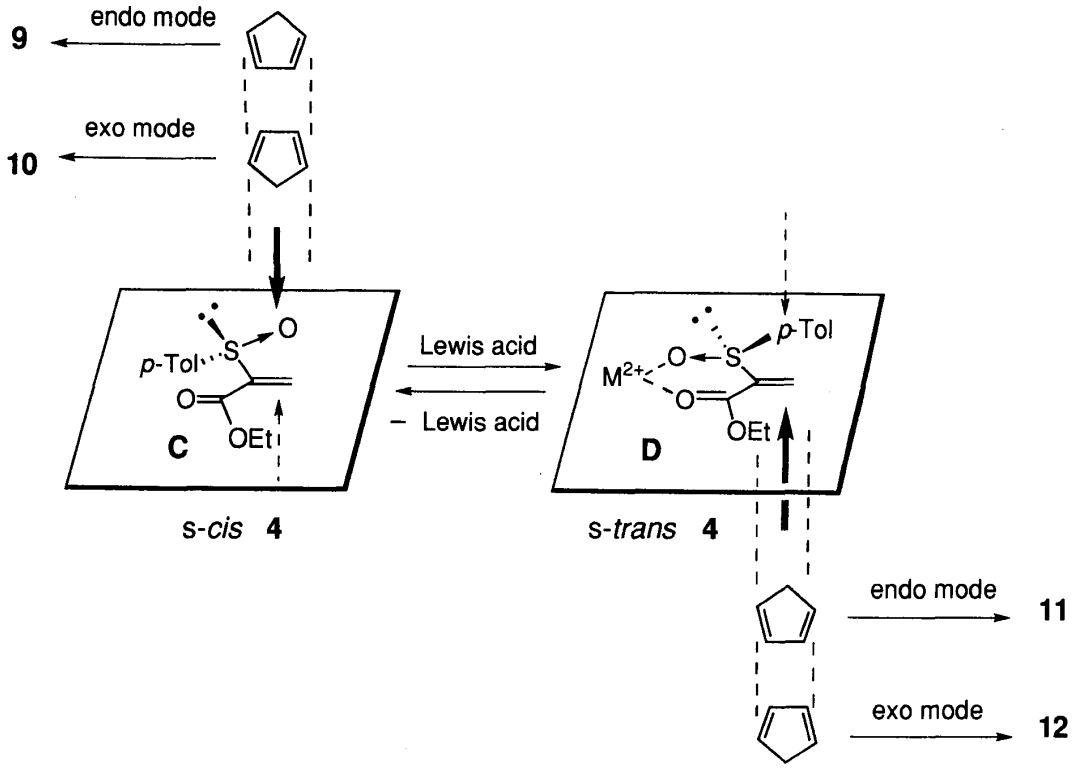
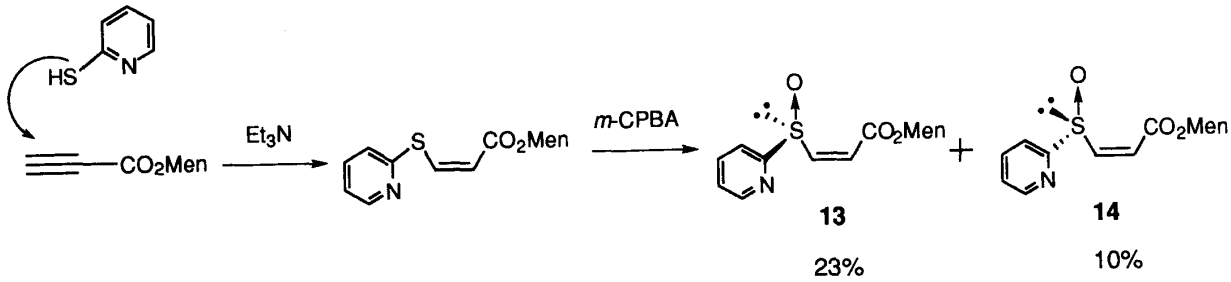


Fig. 2

2. Asymmetric Diels-Alder Reactions Using 2-Pyridyl α,β-Unsaturated Sulfoxides

We have devised the preparation of novel dienophiles by introduction of the alkoxycarbonyl group at α or β position of *p*-tolyl α,β-unsaturated sulfoxides. These dienophiles, however, are

not reactive enough toward a variety of dienes. For example, the sulfoxide 4 does not react with furan under conventional conditions. The fact prompted us to seek a highly reactive Diels-Alder dienophile toward less-reactive diene. Our next approach is to introduce pyridine function in place of a *p*-tolyl group because a 2-pyridyl group has a good electron-withdrawing inductive effect, and we might expect it to activate the C=C bond. The objective dienophile, menthyl 2-pyridylsulfinylpropenoate (**13**) was easily prepared by the reaction sequence shown in Scheme 6.

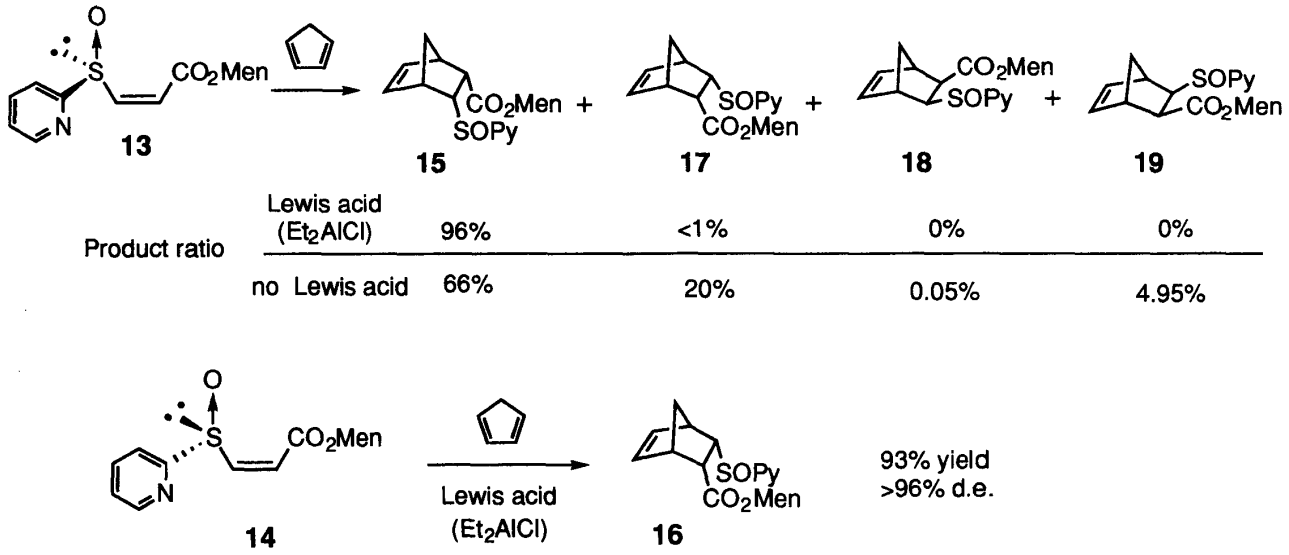


Scheme 6

Although the yields of these diastereoisomeric sulfoxides **13** and **14** are low, the reaction of **13** and **14** with cyclopentadiene proceeds smoothly in the presence of diethylaluminium chloride at -70 ℃, to afford single endo diastereoisomers **15** and **16**, respectively (Scheme 7).[12] When the reaction is conducted at 0 ℃ without the Lewis acid, unsatisfactory selectivity is observed.

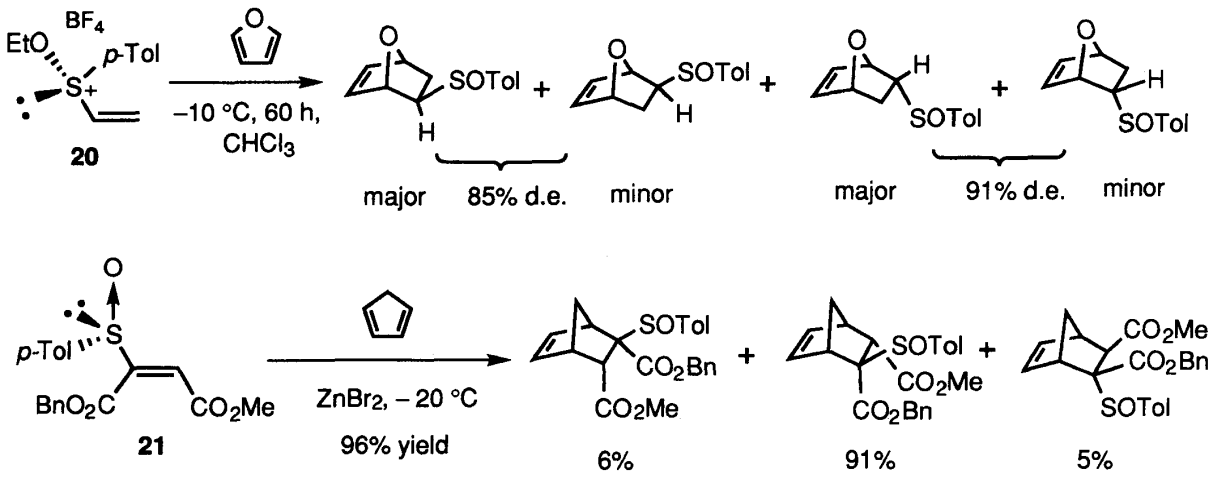
On the other hand the Diels-Alder reaction of **13** with furan proceeds at 50 ℃ for 6 days to give the cycloadducts, albeit with low diastereoselectivity. Upon addition of a Lewis acid, the cycloaddition takes place in a highly diastereoselective manner.

The Diels-Alder adduct **15** has been applied to the synthesis of a common intermediate of biologically important compounds, aristeromycin and neplanocin A.[13]



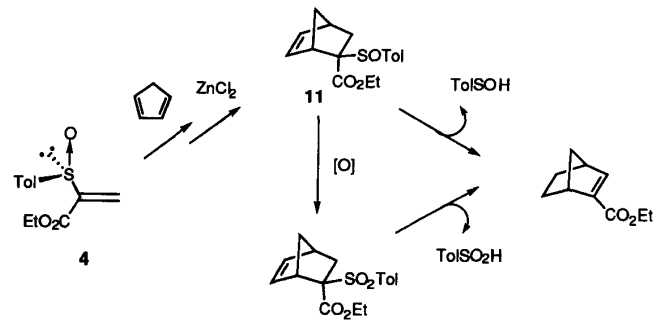
Scheme 7

Concerning facile Diels-Alder reactions with *p*-tolyl α,β-unsaturated sulfoxides, Kagan recently reported that *p*-tolyl vinyl sulfoxide is activated for Diels-Alder reaction by transformation into the corresponding sulfonium salt **20** (Scheme 8).[14] Also investigated was the *p*-tolylsulfinyl maleate derivatives **21** for the Diels-Alder reaction.[15]



Scheme 8

We have described the Diels-Alder reaction by the use of the *p*-tolyl and the 2-pyridyl sulfinyl group as a chiral auxiliary; however, from the viewpoint of asymmetric reactions, there are some weak points in the chemistry of chiral aryl sulfoxides. Namely, i) the chiral auxiliary is lost at a later stage after asymmetric reaction since the sulfinyl group is removed as an unstable sulfenic acid or a sulfinic acid (Scheme 9), and ii) limited kinds of chiral sulfoxides can be prepared by the Andersen method because their synthesis involves carbanionic species such as Grignard reagents.

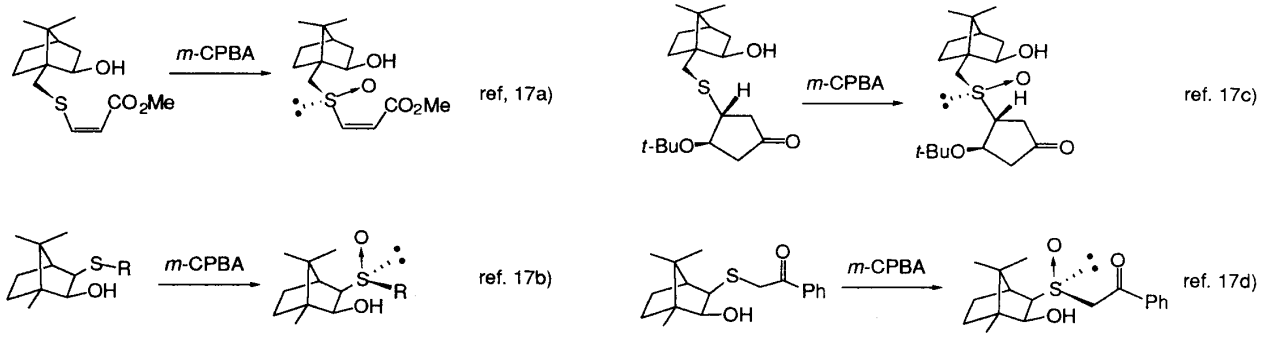


Scheme 9

For the preparation of the chiral sulfoxides, other elegant methods through asymmetric oxidation of prochiral sulfides or by separation of diastereoisomeric sulfoxides have been reported.[16] Nevertheless, the optical purity of the sulfoxides obtained is low in some case and the absolute configuration of the sulfur center appeares to be unpredictable in most cases.

In order to overcome these problems in the chemistry of chiral sulfoxides, we examined a

diastereoselective oxidation of the sulfides derived from camphorsulfonic acid by a directing effect due to the hydroxy fuction in a suitable position. A similar approach based upon camphor-derived sulfides has been employed by other groups (Scheme 10).[17]

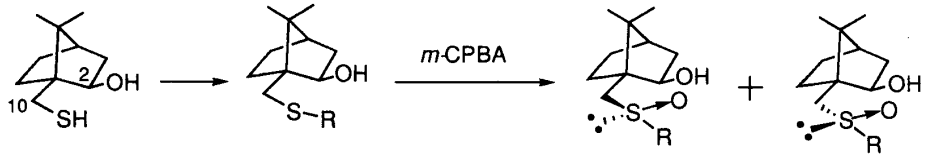


Scheme 10

3. Synthesis of 2-*exo*- Hydroxy-10-bornyl Sulfoxides

We focused on the preparation of the sulfoxides by diastereoselective oxidation of 2-exo-hydroxy-10-bornyl sulfides with *m*-chloroperoxybenzoic acid (*m*-CPBA).

The parent sulfides **23** are easily obtained by coupling of 10-mercaptoisoborneol **22** with alkyl-, alkenyl-, and aryl halide.[18] Sulfides **23** obtained are reacted with *m*-CPBA under mild conditions to give the sulfoxides **24** as the major product. The oxidation with *m*-CPBA proceeds with high diastereoselectivity (Scheme 11). In few cases, the minor diastereoisomeric sulfoxides **25** are obtained by the oxidation. The results are summarized in Table 1.



22 **23** **24** **25**

Scheme 11

Table 1. Results on *m*-CPBA oxidation of sulfides 23

23 (R=)	Yield / %	Reaction time / h	Product ratio (24:25)	d.e. / %
Me	95	1	~100:0	~100
Et	95	2	~100:0	~100
*iso*Pr	89	2	~100:0	~100
Allyl	90	1	~100:0	~100
CH_2Ph	91	1	~100:0	~100
CH_2CH_2Ph	68	3	~100:0	~100
CH_2COPh	68	2	57:9	66

A similar diastereoselectivity in the *m*-CPBA oxidation of some 2-*exo*-hydroxy-10-bornyl sulfides has been observed by De Lucchi *et al.*,[17a] Cinquini *et al.*[17b] and Haynes *et al.*[17c,d]. The absolute configurations of some sulfoxides thus obtained have been established unequivocally by X-ray analysis[17-20], the result of which is rationalized by the mechanism in which the secondary hydroxyl group in the bornyl residue would form a hydrogen bond with the carbonyl group in *m*-CPBA and control the stereochemical outcome in the oxidation.[21]

It is noteworthy that the absolute configuration of the sulfinyl center in these sulfoxides obtained by *m*-CPBA oxidation is predictable. Since the rate of oxidation of sulfides to sulfoxides is generally high, this method would be applicable to the synthesis of chiral sulfoxides with labile, sensitive groups to oxidation under mild or drastic conditions.

3-1. Synthesis and Asymmetric Diels-Alder Reaction of the α-Sulfinyl Maleate Derivative

It is well known that the olefin part in maleic acid diester is quite reactive toward Diels-Alder dienes.[22] However, the preparation of chiral α-sulfinyl maleate derivatives by the Andersen method would require tedius steps with such care as protection of the functional groups. We thought that the application of our synthetic methodology would make a facile chiral synthesis of α-sulfinyl maleates possible.

It should be emphasized that a high level of stereocontrol in Diels-Alder reactions of vinyl sulfoxides can be achieved only when the additional alkoxycarbonyl group is incorporated in the α-position or the (*Z*)-β-position with respect to the sulfinyl group. In the design of a sulfinyl dienophile with two alkoxycarbonyl substituents, the sulfinylmaleate should be preferable to the fumarate congener. That is, the (*Z*)-β-alkoxycarbonyl substituent of the sulfinylfumarate would allow both the s-*cis* and the s-*trans* conformation, while the predominant conformer of the sulfinylmaleate would be defined as s-*trans* due to the dipole-dipole repulsion (Fig. 3). We thus undertook the synthesis of the sulfinylmaleates.

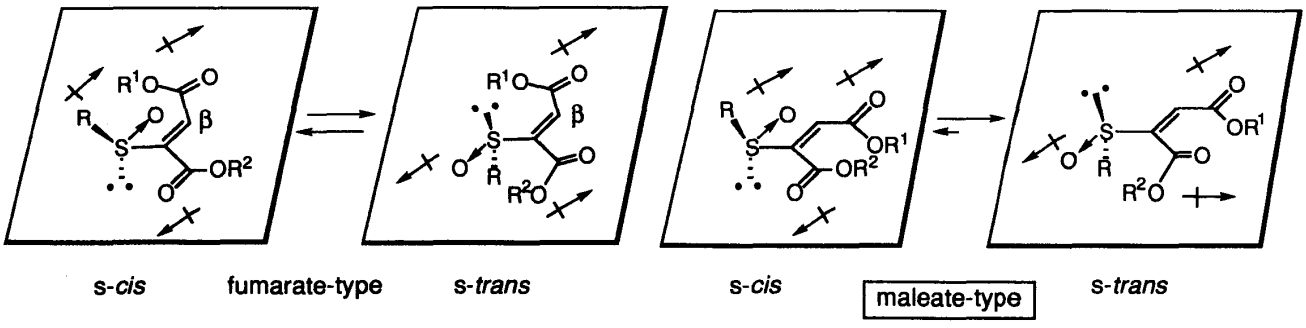
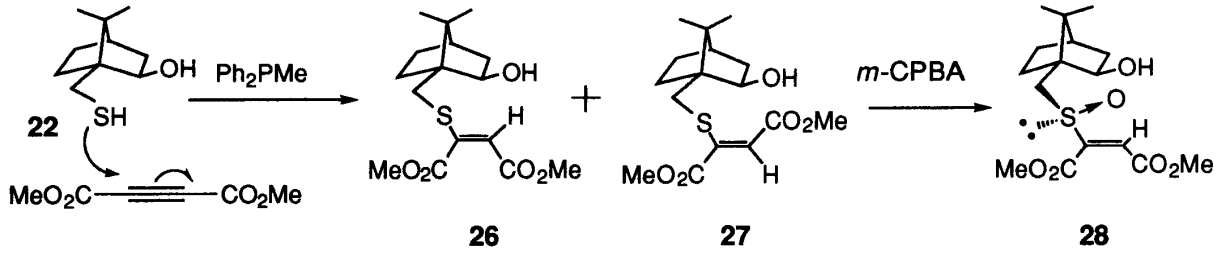


Fig. 3

Of the several routes to the sulfinylmaleates that have been investigated, it was found that the reaction of dimethyl acetylenedicarboxylate with **22** in the presence of Ph_2PMe produces predominantly **26** (**26**:**27** = 4:1) in 93% yield (Scheme 12).[19] These isomers are separable by chromatography. Exposure of **26** to *m*-CPBA affords the sulfinyl maleate **28** as essentially a single isomer.

Fortunately, the fumarate **27** is allowed to react with *m*-CPBA giving the same product **28**, exclusively. The reason for the geometrical isomerization during the oxidation is unclear at present.

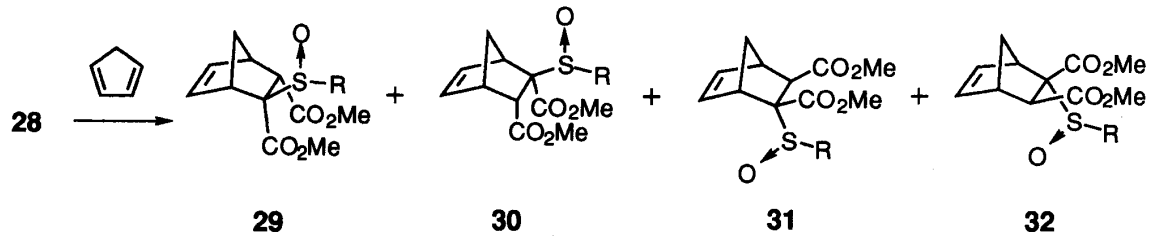


Scheme 12

Diels-Alder Reaction of Sulfoxide **28** with Cyclopentadiene

Table 2 shows the results of the Diels-Alder reaction of **28** with cyclopentadiene under various conditions. In the absence of a Lewis acid, the *exo*-sulfinyl adduct **29** is produced predominantly with high diastereoselectivity (**29**:**30** = 11.7:1). Under the presence of a Lewis acid (= chelation-controlled conditions, entries 2-7), diastereoselectivities of *exo*- and *endo*-sulfinyl adducts are ≈100%. Under the optimized conditions (entry 4), stereoselectivity {(**29**+**30**)/(**31**+**32**)} is very high (15.3:1) as well as diastereoselectivity (0:15.3) for endo addition {**29** vs. **30**}.

The stereochemistry of the adducts **29**-**32** was assigned based upon the mechanism we previously proposed.[11] The structure of the adduct **30** was confirmed by single-crystal X-ray analysis.



Scheme 13

Table 2. Diels-Alder reaction of **28** with cyclopentadiene under various conditions.

Entry	Lewis acid (1.5 equiv.)	Solvent	Temp./ ℃	Product ratio **29**:**30**:**31**:**32**	Yield/%
1	none	CH_2Cl_2	25	11.7:1:0:2.2	87
2	$ZnCl_2$	CH_2Cl_2	0	0:7:1:0	69
3	$ZnCl_2$	toluene	−20	0:8.8:1:0	ND[a]
4	$ZnCl_2$	CH_2Cl_2	−20	0:15.3:1:0	92
5	$ZnCl_2$	CH_2Cl_2	−50	0:8.2:1:0	ND[a]
6	$ZnBr_2$	CH_2Cl_2	−20	0:6.2:1:0	ND[a]
7	Et_2AlCl	CH_2Cl_2	−20	0:3:1:0	ND[a]

[a] ND = not determined

The reversed selectivity of the reaction with or without a Lewis acid can be explained by the mechanism (Fig. 4). Namely, under chelation-controlled conditions, the sulfoxide would exist predominantly in conformation **A** where zinc could coordinate with the sulfinyl oxygen and the ester carbonyl. On the other hand, in the absence of a Lewis acid, the conformer **B**, which becomes more stable than **C** due to the dipole-dipole repulsion, would react with cyclopentadiene predominantly to give the adduct **29**. In both cases, cyclopentadiene should attack the less-hindered lone-pair side of **A** and **B**, giving the adducts **30** and **29**, as the major products, respectively.

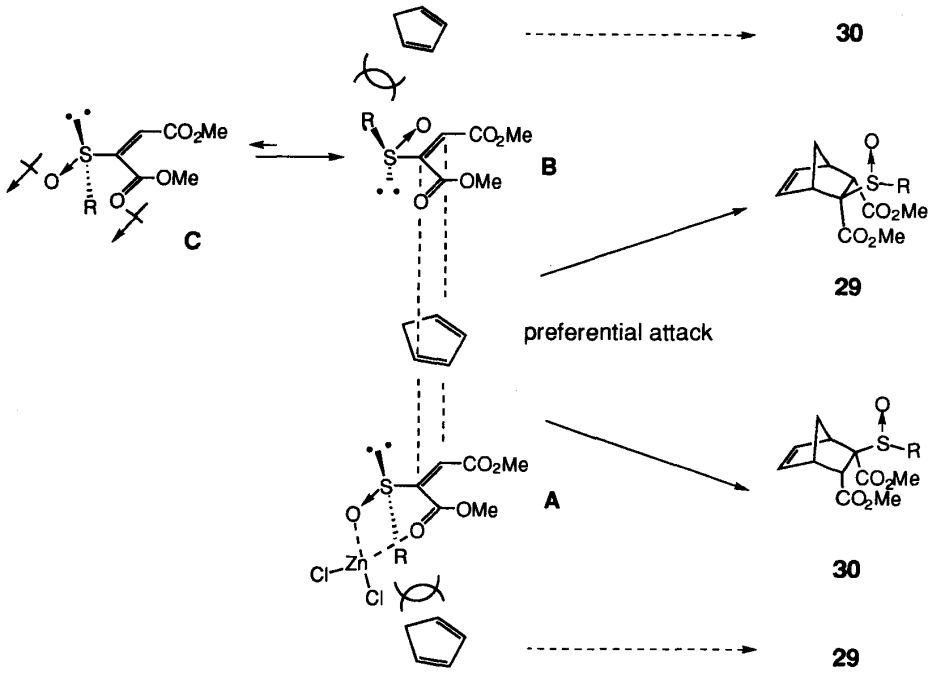
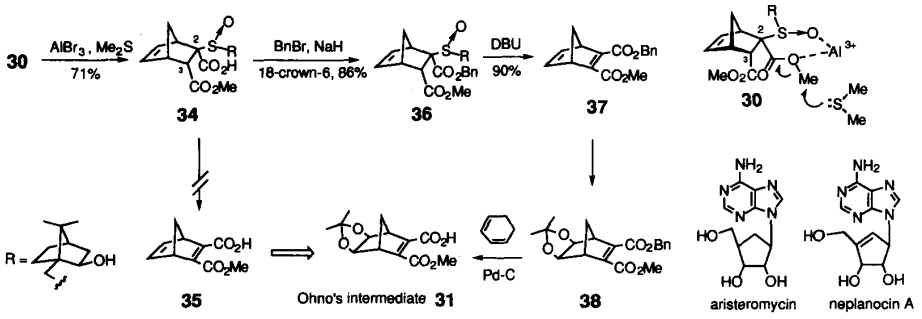


Fig. 4. Stereochemical outcome of the Diels-Alder reaction of **28** in endo mode.

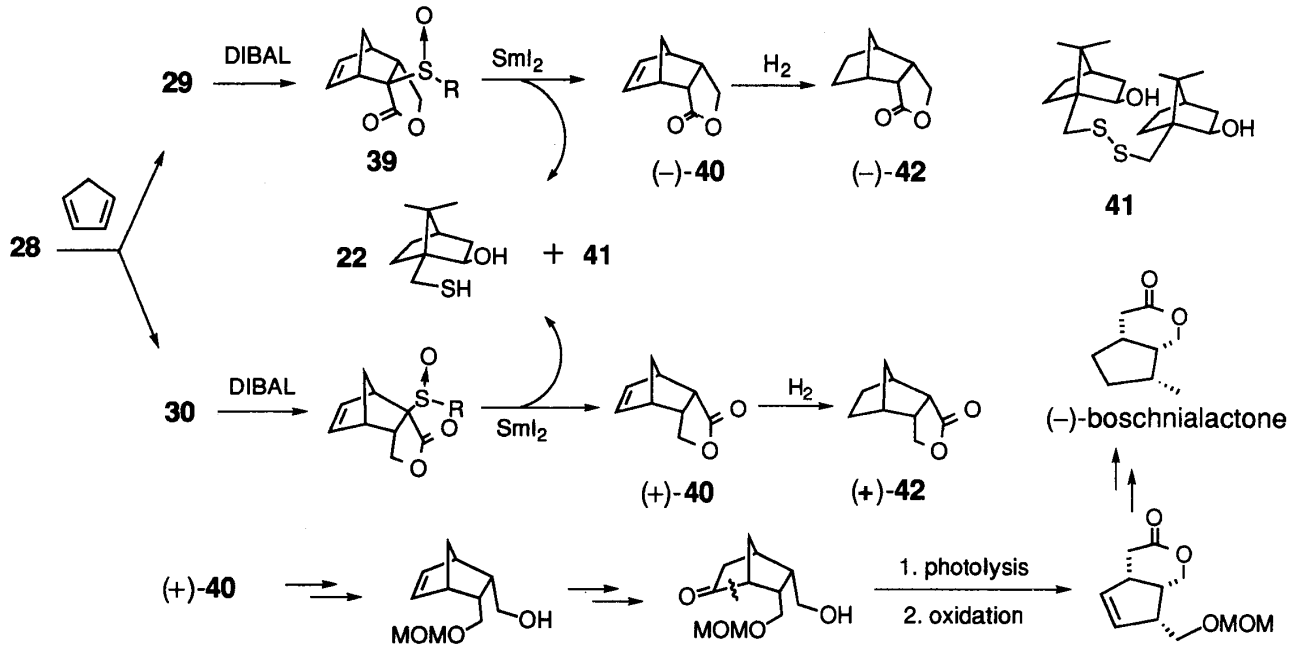
Application to Enantioselective Synthesis of Natural Products

The major Diels-Alder adduct **30** has been converted into the common intermediate **31** in the synthesis of carbocyclic nuleosides, aristeromycin and neplanocin A (Scheme 14).[19] The reaction sequence in the synthesis involves a selective demethylation of **30** by a $AlBr_2$-Me_2S system.



Scheme 14

The adduct **29** is reduced with di-isobutylaluminium hydride (DIBAL) to give the lactone **39** in 61% yield (Scheme 15). Attempts to remove the sulfinyl group in **39** with $TiCl_3$ result in only the recovery of **39**. Deoxygenation using either PBr_3 or Zn-AcOH is also unfruitful. Finally, samarium-induced reduction of **39** affords the lactone (−)-**40** with an efficient recovery of the chiral auxiliary, **22** and the disulfide **41**.[24] Without t-butyl alcohol as a proton source, the disulfide **41** is produced exclusively. In a similar manner, the adduct **30** is transformed into (+)-**40** by the reductions. Lactones (+)- and (−)-**40** are hydrogenated to (+)- and (−)-**42**, which have been reported as a key precursor in the synthesis of the natural product.[23] Thus, we achieved an enantiodivergent synthesis of the lactone **40**, starting from a dienophile **28**. The lactone (+)-**40** has been tranformed into a biologically active terpenoid, (−)-boschnialactone by us.[25]



Scheme 15

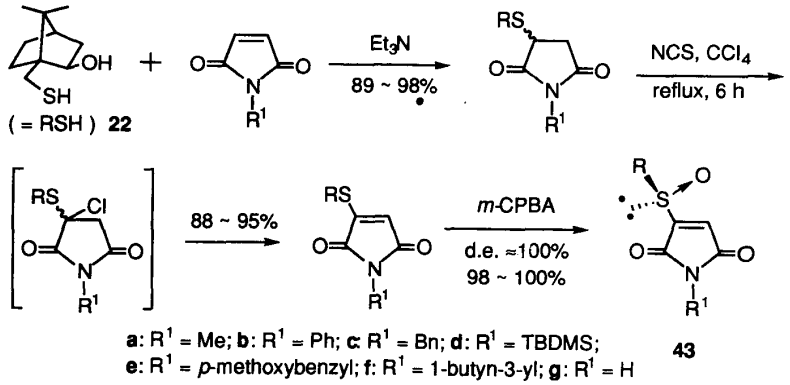
3-2. Synthesis and Diels-Alder Reaction of α-Sulfinyl Maleimide Derivatives

It was found that the dienophile **28** is entirely unreactive toward furan. High-pressure methodology[26] and use of high-pressure effects on cycloadditions using an inorganic salt[27] would affect the Diels-Alder reaction of **28** with furan. To realize the cycloaddition with furan under conventional conditions, and in a practically useful manner, we focused on the high reactivity[22] of the double bond in maleimides which could effect the Diels-Alder reaction.

Synthesis of Chiral Maleimide Derivatives

Chiral α-sulfinyl maleimides **43** can be synthesized in excellent yields from *N*-substituted maleimides and 10-mercaptoisoborneol **22** in a 3-step sequence (Scheme 16).[20] The oxidation with

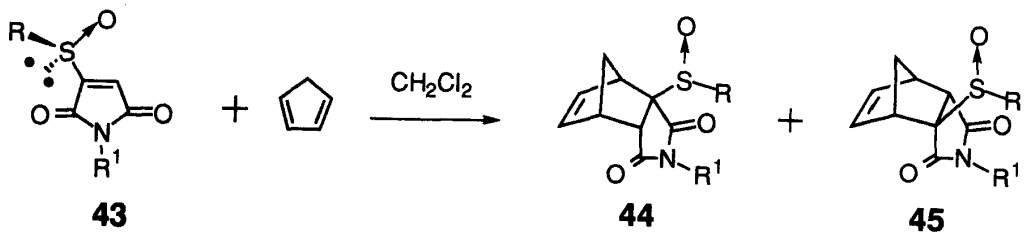
m-CPBA proceeds with high diastereoselectivity (d.e. ≈100%) giving the sulfoxides **43**. Attemps to obtain an *N*-unsubstituted maleimide **43g** by the oxidation of the corresponding sulfide were unsuccessful and resulted in polymerization.



Scheme 16

Diels-Alder reaction of Dienophile **43** with Cyclopentadine

As anticipated, the maleimides **43** were found to be quite reactive toward Diels-Alder dienes. The results of the Diels-Alder reaction of *N*-benzyl derivative **43c** with cyclopentadiene at a variety of temperatures are summarized in Table 3.



Scheme 17

In the presence of $ZnCl_2$, the reactions proceed with high diastereoselectivities to produce the adduct **44c**. In contrast, in the absence of a Lewis acid, the diastereoselectivites are low, and the other adduct **45c** is obtained as the major product. In no case are the *endo*-sulfinyl adducts obtained.

Table 3. Diels-Alder reaction of **43c** with cyclopentadiene

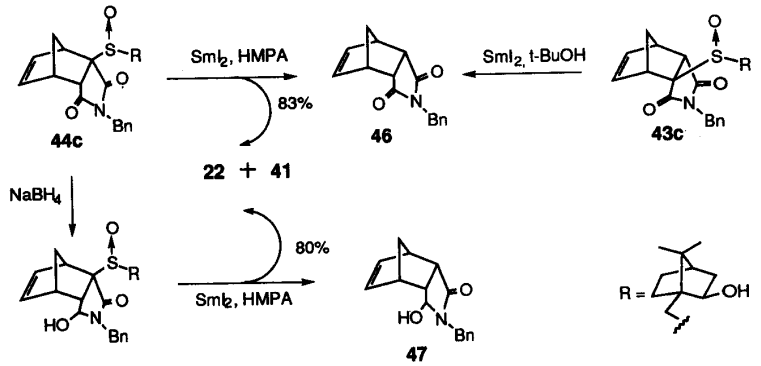
	ZnCl2			no Lewis Acid		
Reaction Temp/ ℃	Time/ min	Yield/%	d.s. **44c : 45c**	Time/ min	Yield/%	d.s. **44c : 45c**
40	5	91	94 : 6	5	≈100	31 : 69
25	20	≈100	97 : 3	60	98	26 : 74
0	20	≈100	97 : 3	60	97	28 : 72
−20	20	≈100	98 : 2	60	99	29 : 71
−78	30	97	97 : 3	60	≈100	36 : 64

Similar results were observed for the Diels-Alder reaction of other sulfoxides **43a**, **43b**, **43d**, **43f** with cyclopentadiene. Some examples are shown in Table 4.

Table 4. Diels-Alder reaction of **43a**, **b**, **d**, **f** with cyclopentadiene

Dienophile	Lewis acid	Reaction Time/ ℃	Time/h	Product ratio by HPLC	Yield /%
43a	none	0	0.5	**44a** : **45a** (27 : 73)	99
43a	$ZnCl_2$	0	0.5	**44a** : **45a** (96 : 6)	95
43b	none	0	0.5	**44b** : **45b** (27 : 73)	98
43b	$ZnCl_2$	0	0.5	**44b** : **45b** (90 : 10)	97
43d	$ZnCl_2$	−80	0.5	**44d** : **45d** (99:<0.5)	93
43f	$ZnCl_2$	−75	0.5	**44f** : **45f** (98 : 2)	93

Both of the adducts **44c** and **45c** are transformed into the known *endo*-imidocarbonyl compound **46** by the action of SmI_2, with recovery of the chiral auxiliary (Scheme 18). The adduct **44c**, whose structure was confirmed by X-ray crystallography, is likewise transformed into the chiral lactam **47** by regioselective reduction with $NaBH_4$.

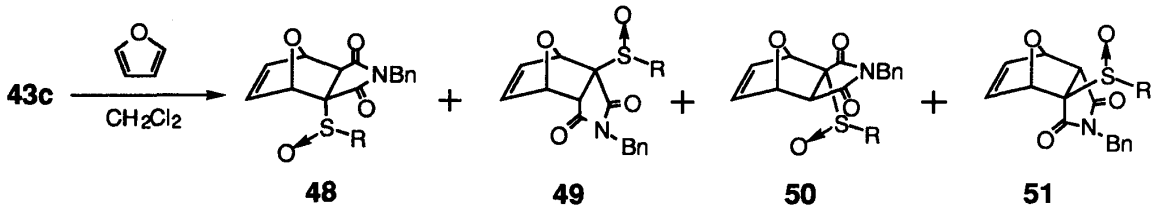


Scheme 18

Diels-Alder Reaction of **43c** with Furan

Next, we examined the cycloaddition of **43c** with furan (Scheme 19). The results are summarized in Table 5. It was found that the product ratios of the adducts derived from the reaction with furan varied depending on the reaction temperature. The reaction conducted at 0 ℃ (entries 2, 3) produces the single diastereoisomers of both *endo*- and *exo*- sulfinyl adducts **48** and **49**. The reaction at room temperature (entry 6) results in the exclusive formation of the *endo*-sulfinyl adducts **48** and **50**, which showed that *exo*-sulfinyl adducts **49** and **51** undergo isomerization to thermodynamically more stable *endo*-sulfinyl adducts **48** and **50** through dissociation and recombination. It is noteworthy that under optimized conditions (entries 4 and 5), the reaction proceeds with high

diastereoselectivities of *endo*-sulfinyl adducts {**48** vs. **50**} and with high exo/endo stereoselectivities {(**48** + **50**) vs. (**49** + **51**)}.

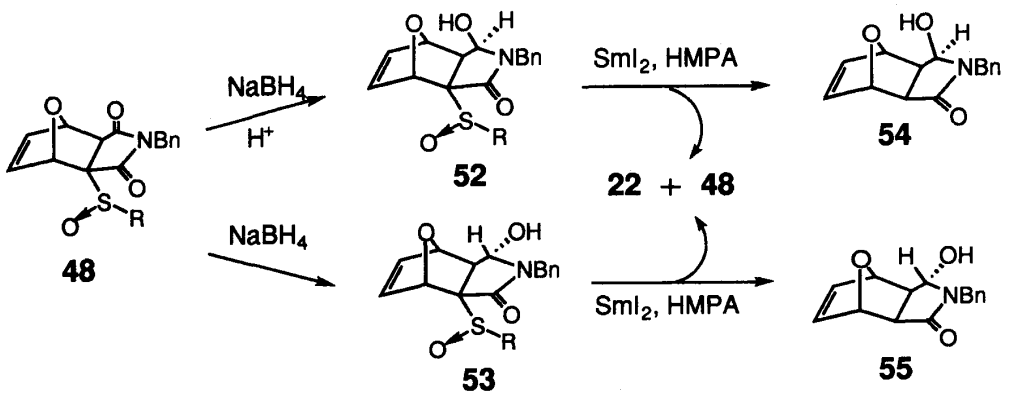


Scheme 19

Table 5. Diels-Alder reaction of **43c** with furan

Entry	Additive (1.5 equiv.)	Temp. / ℃	Time/ h	Product (ratio)	Isolated yield/%
1	$ZnCl_2$	−20	62	**48** : **49** : **50** : **51**	60
				(49 : 26 : 11 : 15)	
2	$ZnCl_2$	0	0.5	**48** : **49** (71 : 29)	66
3	$ZnCl_2$	0	60	**48** : **49** (68 : 32)	72
4	$ZnCl_2$	10	1	**48** : **49** : **50** : **51**	56
				(79 : 9 : 7 : 5)	
5	$ZnCl_2$	10	56	**48** : **49** : **50** : **51**	68
				(80 : 8 : 4 : 8)	
6	$ZnCl_2$	25	20	**48** : **50** (55 : 45)	56
7	none	0	24	**48** : **49** : **50** : **51**	56
				(29 : 22 : 29 : 20)	

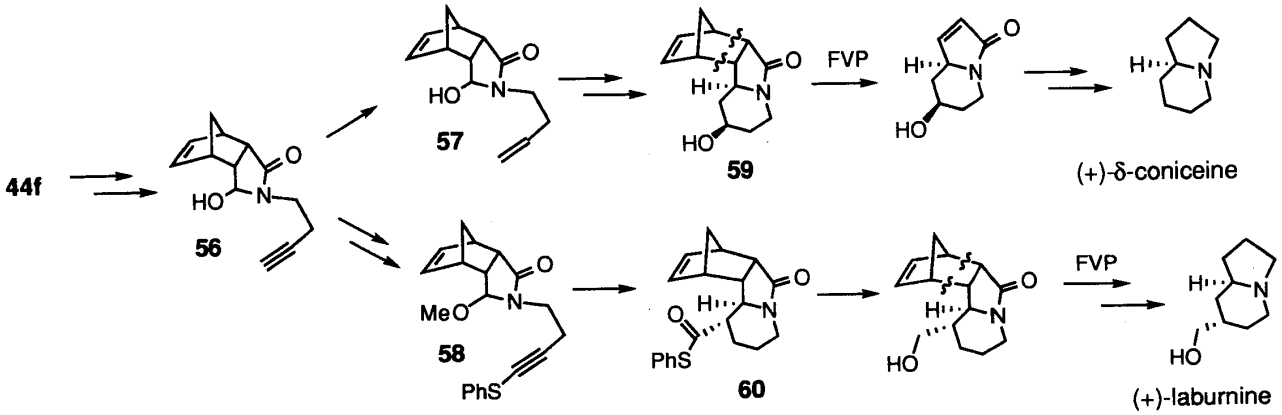
The adduct **48** is converted into **52** by $NaBH_4$ reduction under acidic conditions (Scheme 20). On the other hand, reduction with $NaBH_4$ under basic conditions results in the exclusive formation of **53**. These lactams **52** and **53** are desulfinylated with SmI_2 to lead to **54** and **55**, respectively.



Scheme 20

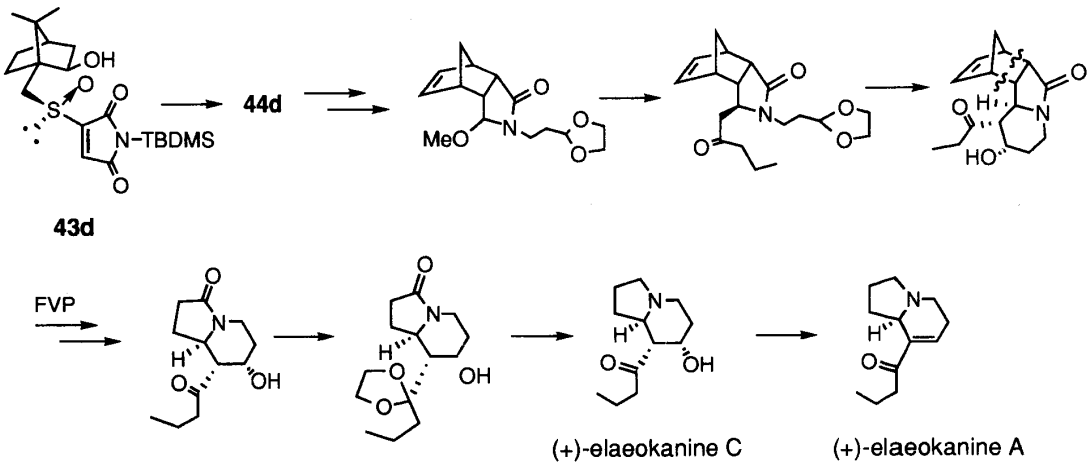
Application to Natural Products Synthesis

The chiral lactams **47**, **54** and **55** would be useful precursors for the synthesis of nitrogen-containing natural products on the basis of *N*-acyliminocyclization strategy.[28] The application of this methodology has been successfully applied to the enantioselective synthesis of bicyclic alkaloids (Scheme 21). Reduction of the Diels-Alder adduct **44f** with $NaBH_4$ followed by desulfinylation affords the lactam **56**. The tetracyclic amides **59** and **60**, obtained by *N*-acyliminocyclization of **57** and **58**, respectively, have been further transformed through flash-vacuum pyrolysis into (+)-laburnine and (+)-δ-coniceine.[29]



Scheme 21

Starting with the adduct **44d** derived from the Lewis acid-promoted Diels-Alder reaction of *N*-TBDMS-maleimide **43d** with cyclopentadiene, we succeeeded in the enantioselective synthesis of (+)-elaeokanine A and (+)-elaeokanine C *via* flash vacuum pyrolysis (Scheme 22).[30]



Scheme 22

Conclusion

This review has described that the use of a 2-*exo*-hydroxy-10-bornyl group as a chiral sulfinyl ligand realizes the facile preparation of chiral sulfoxides. Especially, the chiral α-sulfinyl maleate and α-sulfinyl maleimides, obtained by synthetic methodology, provide efficient

dienophiles that effect the asymmetric Diels-Alder reactions with a high degree of diastereoselectivity. Moreover, it should be emphasized that the absolute configuration of the sulfinyl center in these sulfoxides is predictable, and the chiral auxiliary, 10-mercaptoisoborneol, can be easily recovered by the action of samarium diiodide. The methodology using chiral α,β-unsaturated sulfoxides will continue to add a new feature to the usefulness of asymmetric Diels-Alder reactions.

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